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㉙ Hair strengthening and permanent waving composition.

㉚ Composition for strengthening hair and for imparting a
permanent configuration thereto comprising an alkyltrialkoxy-
silane and a solvent.

EP 0 159 628 A2

HAIR STRENGTHENING AND PERMANENT WAVING COMPOSITION

1 This invention relates to hair strengthening and permanent waving compositions, and more particularly, to reactive silicone hair strengthening and waving compositions.

5 Hair care is one of the most important parts of 5 beauty care, and a large variety of hair treatment products are used for providing such care in the form of pre-shampoo conditioners, shampoos, after-shampoo conditioners, rinses, setting lotions, sprays, dyes, bleaches, permanent wave agents and the like. These products in addition to providing 10 the desired result in the hair, such as luster, curl combability, softness, color and an overall appealing look, also do damage to the hair, especially when used indiscriminantly without professional guidance. Damage to hair may also result from other sources, such as combing, 15 humidity, dryness, dirt, sunrays, such as u.v. and infrared radiation, and pollution in the atmosphere. However, damage to hair occurs mostly in the form of physical and chemical changes in hair as a result of bleaching, oxidative dying, hair relaxing via alkaline relaxers and reducing waving and 20 curling preparations.

25 Hair damage may occur slowly and in various ways with frequent "treatment" of the hair. Over an extended time period the use of various chemicals in the hair treatment products will effect a weakened hair structure. Illustrative of this undesirable effect is that which occurs when the natural configuration of hair is altered from curled to straight or vice versa. The hair is subjected to the action of a composition which relaxes the hair by rupturing the 30 disulfide bonds in the keratin of the hair to produce free sulfhydryl groups. This breakage in the disulfide diminishes

1 the rigidity of the hair proteins, leaving the hair pliable
and soft. The compositions most commonly used as relaxers
are based on sodium hydroxide, sulfite, or thioglycolate.
When a thioglycolate based composition is used as the
5 relaxer, the hair is treated with an oxidant, such as
peroxide, to impart rigidity to the hair. These operations,
particularly the reduction step, can be carried out at either
room or elevated temperature. Both types of treatment, the
cold as well as the hot, require visual evaluation of the
10 hair. Ultimately, the quality of the hair, straightened or
curled, rests on the subjective judgement of the salon
operator, and more often than not because of the subjective
element, the hair is either underprocessed or overprocessed.

15 In addition to the problem of being underprocessed
or overprocessed, the hair subjected to oxidative hair
preparations, lacks the desired texture, it is raspy,
troublesome to comb, and require further conditioning. To
correct these conditions some manufacturers of hair treatment
products frequently supply post-treatment conditioners
20 usually as part of a kit included with the acidic oxidative
preparation. Others incorporate specific hair conditioning
agents compatible with the oxidizing agents, such as
non-ionic and cationic agents.

25 Hair conditioning agents are used not only in
conjunction or after treatment with oxidizing agents but also
to generally assist in the control and management of hair as
for example after shampooing. Conditioned hair is easily
untangled and combed through after shampooing, lays orderly
when dry and provides a favorable feeling to the touch. The
30 conditioning action on hair, particularly by cationic
conditioning agents, is believed to be caused by the
attraction of the positively charged agent to the negative
sites on hair protein resulting in the deposition of the
agent on to the hair fiber.

1 Cationic agents or surfactants have been used
extensively as hair conditioning agents in creme rinses and
shampoos. Best results have been obtained with cationic
surfactants that are long chain high molecular weight
5 quaternary compounds or long chain fatty amine salts. The
positive charge of the quaternary surfactant is attracted to
the negatively charged surface of the hair protein giving it
lubricity during wet combing and a desirable texture after
drying.

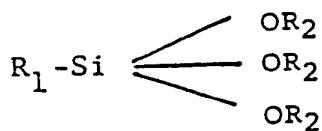
10 Other types of agents for deposition on hair used
in the prior art are the organo silicones. The organo
silicones, having hydrolyzable groups on the silicon atom,
hydrolyze to the corresponding silanol and condense to an
organo-silicone polymer on the hair fibers coating the same
and providing body thereto are used for both conditioning and
15 setting the hair.

20 While the above mentioned conditioning agents
provide substantial benefits to hair, none is directed to
strengthening the hair structure and thereby restore the
hair, as much as possible, to its natural strength.

25 The foregoing discussion illustrates some of the
problems associated with hair care and solutions provided
therefor by the prior art.

30 The present invention addresses the problem of
treating the weakened hair, whether such condition is caused
by nature, the environment or hair treatment preparations
applied thereto.

The present invention relates to a composition for
strengthening the tensile strength of hair comprising
a, an alkyltrialkoxy silane having the formula



wherein

1 R_1 is an aliphatic radical of $C_1 - C_{18}$ carbon atoms, such as methyl, ethyl, propyl, butyl, hexyl, octyl, decyl, octadecyl; substituted aliphatic radicals selected from the group consisting of 3-aminopropyl,

5 N,N -diethyl-3-aminopropyl, and N -(propyl) urea; and an alkenyl radical, such as vinyl and allyl;

10 R_2 is an aliphatic radical of $C_1 - C_4$ carbon atoms, such as methyl, ethyl, propyl and butyl;

15 b, a solvent for said alkyltrialkoxysilane. The solvent may consist of water, ethanol, isopropyl alcohol, nonoxynol-4, or an aqueous solution of ethanol, isopropyl alcohol or nonoxynol-4.

20 To obtain a composition according to the present invention, a solution is prepared by adding an alkyltrialkoxysilane to the appropriate solvent with mixing. The composition preferably comprises about 0.5 to 40% v/v and more preferably 2 to 10% v/v of an alkyltrialkoxysilane in the solvent. The preferred solvent is an aqueous solution of ethanol, isopropyl alcohol or nonoxynol-4 in which the water constitutes no more than about 20% v/v of the total solvent volume.

25 Although the silanes described herein are stable for several days in alcohol/water phases having from 0 - 20% water, it is preferred to prepare the solution just prior to application to the hair. If the solution is allowed to stand in the presence of water for prolonged time periods, excessive polymerization and premature precipitation of the silane may occur, thus rendering the composition less effective for its intended use.

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1 The method of application of the composition
includes applying the composition to the hair by submerging
the clean hair in the composition or applying the composition
with an applicator and working it into the hair with the
fingers and a comb. The process is completed by blow drying
5 the hair with hot air.

10 The present invention is based on the discovery
that the reactive alkyltrialkoxysilane containing three
labile alkoxy groups in the presence of water hydrolyzes to
form three reactive silanol groups which in turn condense
with each other to form oligomers. The oligomers then
hydrogen bond with functional groups containing active
hydrogens (hydroxyl, amino, carboxyl, sulfhydryl and the
like) in the hair. During drying or curing a stable covalent
15 bond is formed with the hair with concomitant loss of water.
While the curing process will occur at room temperature, it
is preferred to speed up the reaction by drying the hair with
a hot air dryer. The application of heat speeds up
evaporation of the solvent and the by-products of the
reaction. Once water has been removed from the hair, the
20 resulting bonds become stable to hydrolytic action. The
degree and rate of polymerization of the silane is determined
by the amount of water available and the organic substituent
of the silane.

25 This characteristic of the silanes of the present
invention allows for their application to hair for increasing
hair strength, retaining hair configuration such as curls,
and providing manageability to hair.

30 The silanes of the present invention are either
commercially available or can be prepared by methods known in
the art using commercially available starting materials and
reagents.

1 Silanes are readily solubilized in ethanol,
1 isopropyl alcohol and many other organic solvents, however,
for the present invention the preferred solvent for the
silanes is an aqueous/alcohol mixture containing up to 20% by
5 volume of water. This composition ensures that a sufficient
amount of water is available to hydrolyze the silane and
possibly swell the hair fibers for increased penetrations of
the active ingredient prior to the polymerization step.
Silanes show unexpected stability to water in such vehicles
10 as determined by the time to hazing (precipitation of
siloxane polymers). For example, solutions of
ethyltriethoxysilane dissolved in 80/20 ethanol/water remain
clear for several days. As the percentage by volume of water
increases beyond 20% of the total solvent composition, more
15 rapid hazing and precipitation of the siloxane polymer is
observed to occur, thus rendering the composition less
effective for its intended use.

Test methods used in connection with the invention
and working examples follow.

20 Tensile Strength

This test relates to the determination of the force
required to break (tensile strength at breakpoint) the hair
sample by using a constant elongation rate tester such as the
Instron Tensile Tester. The test is performed as follows:

25 Each tress of hair to be tested is conditioned in a
50% relative humidity chamber for at least 24 hrs prior to
use. Twenty strands of hair, randomly selected from each
tress, are used for the test. A two-inch long section is cut
from each hair strand and weighed to the nearest 0.1
30 microgram. The weighed cut sections are placed into
distilled water and allowed to hydrate for at least 16 hours.

1 Each hydrated hair sample is placed between the jaws of the
Instron Tensile Tester, which are preset at 1 inch apart,
and clamped securely. The tensile strength is then determined
according to the manufacturer's instructions.

5 The tensile strength is the force required to break
the hair strand. This force is expressed in terms of grams
force per cross sectional area of hair strand.

Method For Determination of Silane Content in Hair

10 The silicon content of treated hair is determined
colorimetrically as silicomolybdate or as molybdenum blue and
the result calculated as silane. Approximately 0.7 gram \pm
0.1 mg of hair is weighed accurately into a beaker, to which
5 ml of concentrated nitric acid is added. The sample is
heated to dryness and the addition of nitric acid and heating
15 steps are repeated until a white residue remains in the
beaker. Then 10 ml of 1:10 hydrochloric acid is added to the
beaker and the content is filtered with suction through a
membrane filter. The beaker is thoroughly washed with 1:10
hydrochloric acid and the liquid is filtered. The filter is
placed in the bottom of a polyethylene beaker and 1.0 ml of
20 hydrofluoric acid is added to cover the filter. The beaker
is then covered and allowed to stand for 30 min. Then 25 ml
of water and 50 ml of boric acid solution is added with
stirring, and the solution is heated at 40°C in a water bath
for at least 10 min. Four (4) ml of molybdic acid reagent is
25 added while stirring. Then 20 min. later, 20 ml of 10N
sulfuric acid is added with stirring. If any yellow color
persists, the solution is read within 2 min. after
acidification in a spectrophotometer at 420 nm against
distilled water. If a colorless solution results, the
30 solution is allowed to stand for 2 to 5 min. and 1 ml of
1-amino-2-naphthol-4-sulfonic acid reagent is added, which
is then mixed and read after 20 min. at 820 nm.

1 A calibration curve in the yellow silicomolybdate
concentration range (420 nm) is made by diluting 0.5, 1, 2
and 3 ml aliquots of the stock silicon (1mg/ml) standard to
25 ml in polyethylene beakers and proceeding as hereinbefore
5 described from and including the step of heating the solution
for at least 10 min. After completing the steps as
indicated, absorbance is read at 420 nm. Absorbance against
mg silicon is then plotted. A calibration curve is also
prepared in the molybdenum blue concentration range (820 nm)
10 by diluting 50, 100, 200 and 500 microliters of the silicon
stock standard (1mg/ml) to 25 ml in polyethylene beakers and
proceeding as described above for the silicomolybdate
calibration curve. Absorbance is read at 820 nm.

15 The concentration of silicon is obtained from the
appropriate calibration curve. The calculation is as
follows:

$$\text{Percent silane} = \frac{\text{mg silicon}}{\text{grams of hair}} \times \frac{\text{mole weight of silane}}{\text{atomic weight of silicon}} \times 0.1$$

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EXAMPLE 1

1 A hair sample previously weakened by sodium hydroxide was submerged in 3.0% v/v solution of ethyltriethoxysilane (obtained from Petrarch Systems, Inc., Levittown, PA) in a mixture of 80/20 ethanol/water. The hair 5 was rinsed free of excess silane and cured by blow drying with a hot air dryer for about ten minutes. The hair was tested using the above-described test procedures. The results were as follows:

10 a. The hair treated with sodium hydroxide solution showed 11 to 14% decrease in tensile strength;

b. The sodium hydroxide weakened hair which subsequently was treated with the silane-containing composition increased in tensile strength back to within 97 to 98% of its original (untreated) tensile strength;

15 c. The silane treated sodium hydroxide weakened hair picked up between 0.4 to 1.4% silicon by weight, calculated as ethyltriethoxysilane.

EXAMPLE 2

20 A 95% v/v solution of ethyltriethoxysilane in nonoxynol-4 was prepared. Immediately prior to treating the hair, 40 parts of the silane/nonoxynol-4 phase was added with stirring to 60 parts of water. The hair, which was previously weakened by sodium hydroxide was completely wetted with the silane/nonoxynol-4/water solution. The solution was 25 allowed to remain on the hair for 30 minutes. The hair was rinsed free of excess solution and blow dried with a hot air drier.

30 Upon testing, the data showed a 10% increase in tensile strength of the hair.

EXAMPLE 3

1 A swatch of virgin hair was heavily damaged by a 45
minute treatment with a 2% aqueous solution of sodium
hydroxide. The alkali-damaged swatch was washed with a pH
5.0 shampoo to restore the acid balance, allowed to dry under
5 ambient conditions and subdivided into a series of
equal-sized tresses. Three tresses were selected and each
treated for 30 minutes with 10 grams of the silane-containing
10 composition of Example 2, cured and blow dried. The
procedure used to treat the three tresses was exactly the
same except for the manner in which the excess silane was
removed. Instron analyses were carried out on all of the
tresses. The result and the manner of removing excess silane
are shown in Table I.

15 Table I
Instron Results for Prepared Tresses

	<u>Sample</u>	<u>n</u>	<u>Tensile Strength (G)</u>	
			<u>\bar{X}^*</u>	<u>SEM**</u>
20	Control virgin hair	20	29.49	± 0.61
	Control alkali-damaged hair	20	14.48	± 1.07
25	Alkali-damaged hair, silane treated, rinsed, then cured	20	17.51	± 0.56
	Alkali-damaged hair, silane treated, cured, then rinsed	20	16.56	± 0.59
30	Alkali-damaged hair silane treated, cured, then rinsed and shampooed	20	16.95	± 0.702

n denotes the number of determinations here and in subsequent tables.

\bar{X}^* denotes the mean of the number of measurements here and in subsequent tables.

35 SEM** denotes the standard error of the mean here and in subsequent tables.

1 The data in Table I show that all the silane
treated tresses have significantly increased in strength
(about 15-20%) relative to the alkali-relaxed control. No
5 significant difference in hair strength is shown among the
silane-treated tresses indicating that the mode by which
excess reagent is removed from the hair has no affect on hair
strength.

10 It was also discovered that if hair, arranged in a
desired configuration with curling rollers or rods, is
treated with a silane-containing composition of the present
invention and blow dried, the silane bonding to the hair not
only increases hair strength but also maintains the hair in
the shape in which it was dried. This effect is shown for
15 both alkali-weakened and virgin hair. The resulting
permanent wave resists the tendency to revert to the initial
configuration even after repeated shampooing.

EXAMPLE 4

20 A dark brown virgin hair swatch obtained from a
single lot was washed with a 10% sodium lauryl sulfate
solution, rinsed with tap water, and blow dried at room
temperature. The swatch was subdivided into eighteen tresses
ten inches long each weighing one gram. One tress was
selected to serve as virgin control and five other were set
aside for silane treatment. The remaining twelve tresses
25 were set aside for the alkali treatment. Before treatment,
each tress was gently combed and separately rolled on curling
rods. Alkali treatment was carried out by submerging the
rolled tresses in a 2.0% sodium hydroxide solution for one
hour. Subsequently, each tress was rinsed under running tap
30 water for at least 10 minutes. The rolled tresses were towel
dried, soaked in pH 7.0 buffer for one hour to restore the
acid balance, and rinsed out thoroughly to remove the buffer.
The rolled tresses were finally dried at room temperature.

Equimolar solutions of silanes denoted in Tables II
1 and III were prepared separately in a mixture of 80:20
ethanol/H₂O, to carry out silylation. The virgin and alkali
treated tresses on rollers were treated separately for 30
5 minutes with 100 ml of 0.26M solution of silane. The rolled
tresses were blow dried for four minutes after the silane
treatment with a 1600-watt blow drier and thoroughly sprayed
with water. The rolled tresses were allowed to stand for
five minutes and finally blow dried for 15 minutes at the
10 high temperature setting. Unsilylated virgin and alkali
control were also subjected to the same treatment. The hair
tresses, after equilibrating to room temperature, were
carefully unwound from the curling rods and mounted on the
curl retention board. The mounted specimens were then
15 incubated at 100°F/95% relative humidity. Curl retention
data were obtained periodically over 24 hours. The tresses
were removed from the board, wetted under running tap water
for 1 minute, dried and soaked in a beaker of water for 30
additional minutes, removed, air dried, twice shampooed and
20 rinsed again. The final curl length and patterns of each
tress were evaluated to determine curl stability. Data and
comments are summarized in Tables II and III.

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Table II
Alkali Pre-Treated Hair

<u>Sample</u>	<u>Silane (1) Conc. (%)</u>	<u>n</u>	<u>% Curl Retention (X)</u>	<u>SEM</u>	<u>Comments</u>
Control (alkali relaxed)	0.00	2	12.27	± 1.35	Good curl and S-wave pattern No shine
Octadecyl triethoxysilane	10.84	2	14.55	± 0.13	Very good S-wave pattern Good shine
3-Aminopropyl triethoxysilane	4.70	2	17.80	± 0.20	Very good S-wave pattern Good shine
N-(triethoxy silylpropyl)urea	6.90	2	16.36	± 0.42	Very good curl and S-wave pattern

(1) All solutions contain equal moles of silanes (0.26M)

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Table - III
Virgin Hair

<u>Sample</u>	<u>Siilane (1) Conc. (%)</u>	<u>n</u>	<u>% Curl Retention (x)</u>	<u>Comments</u>
Control virgin hair	0.00	1	7.16	Almost no curl, no S-wave pattern
Octadecyltriethoxy- silane	10.84	1	12.73	Very good body wave
Octyltriethoxy- silane	7.20	1	11.04	Fair body wave
3-Aminopropyltri- ethoxysilane	4.70	1	11.35	Good body wave
Vinyltriethoxy- silane	4.90	1	11.94	Good body wave
N-(triethoxy- silylpropyl)urea	6.90	1	10.38	Fair body wave

(1) All solutions contain equal moles of silanes (0.26M)

EXAMPLE 5

1 Series of tresses were prepared from a single lot
of dark brown virgin hair, each tress being 1.5 ± 0.1 g in
weight and 10" long. Two of the tresses, selected at random
5 to serve as permanent waved controls, were treated with
Collagen Amino Acid Professional Formula [®] (active
ingredients: 9.2% ammonium thioglycolate, 10% sodium
bromate). Fourteen virgin hair tresses were wrapped on rods
and immersed for 1 hour in a 2% sodium hydroxide solution.
10 The wrapped tresses, after having been rinsed free of alkali,
were treated with pH 7.0 buffer to restore the acid balance
to the hair. The tresses were rinsed free of buffer and
treated as described in Tables IV and V. The procedure used
for the evaluation and curing of alkali-treated hair was
15 described in Example 4. Heat was also applied to the control
samples for an identical period of time. All the prepared
tresses were allowed to equilibrate under ambient conditions
of temperature and humidity.

20 After equilibration, the tresses were carefully
unwound from their curling rods and their respective curl
lengths carefully measured to the nearest 0.1 cm. The
tresses, after having been mounted on a curl retention panel,
were incubated for 24 hours at 100°F/95% RH. Next, the
25 tresses were removed from the panel, flushed with running tap
water for 1 minute, soaked in a beaker of water for 30
additional minutes, removed and shampooed twice the Flex
Shampoo [®], rinsed free of soap and allowed to air dry. The
final curl length and pattern of each tress were carefully
evaluated to determine curl stability.

30 Results are shown in Tables IV and V.

Table - IV

Curl Retention

<u>Sample</u>	<u>n</u>	<u>% Curl Retention (X)</u>	<u>SEM</u>	<u>Comments</u>
Alkali relaxed control	1	10.2	-	Little curl - no S-wave pattern
Alkali relaxed/5% ETES1	1	15.4	-	Good S-wave pattern
Alkali relaxed/30% ETES1	1	15.0	-	Good S-wave pattern
Alkali relaxed/urea swelled-30% ETES1	1	13.4	-	Good S-wave pattern
Alkali relaxed/salt swelled-30% ETES1	1	14.2	-	Good S-wave pattern
Alkali relaxed/30% ETES1 in DET2	2	15.2	<u>+0.20</u>	Very good S-wave pattern
Alkali relaxed/30% ETES1 in DMF3	2	14.1	<u>+0.20</u>	Very tight curl
Permanent waved controls	2	16.7	<u>+0.60</u>	Very good S-wave pattern

(1) ETES = Ethyltriethoxysilane in 80/20 alcohol/water in here and in Table V

(2) DET = Diethyltoluamide

(3) DMF = Dimethylformamide

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Table - V

<u>Sample</u>	<u>n</u>	<u>% Curl Retention (x)</u>	<u>SEM</u>	<u>Comments</u>
Virgin hair control	2	6.9	± 0.60	Very little curl, no S-wave pattern
Virgin hair/5% ETES	2	12.2	± 0.80	Good body wave
Virgin hair/salt swelled 5% ETES ¹	2	12.6	± 0	Good body wave
Virgin hair/urea swelled 5% ETES ²	2	12.6	± 0	Good body wave
Alkali relaxed control	2	7.5	± 0	Very little curl, no S-wave pattern
Alkali relaxed/5% ETES	2	12.2	± 0	Good S-wave pattern
Alkali relaxed/urea swelled 5% ETES	2	11.4	± 0	Good S-wave pattern
Alkali relaxed/salt swelled 5% ETES	2	10.4	± 1.00	Fair S-wave pattern

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(1) Hair was swelled with a 2.8M LiCl/0.5M Na₂SO₄ aqueous solution prior to treating the hair with silane.

(2) Hair was swelled with a 4M aqueous solution of urea prior to treating the hair with silane.

1 Table IV demonstrates that silylation of alkali
treated hair on curling rods produces a curl pattern
equivalent to that produced by a conventional permanent
waving treatment, and is substantially greater than the curl
produced in the alkaline relaxed control. Curl "memory" was
5 retained in the alkali-silylated tresses even after repeated
shampooing.

10 Table V demonstrates that silane compositions of
the present invention impart a good stable curl to alkali
treated hair and, in addition, that the curl retention of the
virgin hair is significantly improved after silylation
through the formation of a stable body wave pattern.

15 It will be understood that modifications and
variations may be made without departing from the spirit and
scope of the novel concept of the present invention.

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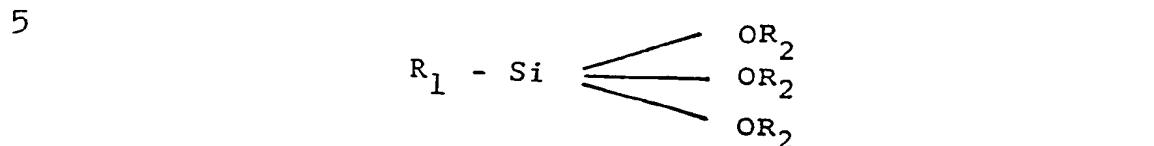
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WHAT IS CLAIMED IS:

1 1. A composition for strengthening the tensile strength of hair comprising:
 a., an alkyltrialkoxysilane having the formula



wherein

10 R_1 is an aliphatic radical of $\text{C}_1 - \text{C}_{18}$ carbon atoms; substituted aliphatic radicals selected from the group consisting of 3-aminopropyl, N,N-diethyl-3-aminopropyl, N-(propyl)urea and alkenyl;

15 R_2 is an aliphatic radical of $\text{C}_1 - \text{C}_4$ carbon atoms; and

 b., a solvent for said alkyltrialkoxysilane.

 2. The composition of claim 1 wherein the aliphatic radical is methyl, ethyl, propyl, butyl, hexyl, octyl, decyl or octadecyl.

20 3. The composition of claim 1 or 2 wherein the alkenyl is vinyl or allyl.

 4. The composition of any of claims 1 to 3 wherein the solvent is water, ethanol, isopropyl alcohol or nonoxynol-4.

25 5. The composition of any of claims 1 to 3 wherein the solvent is an aqueous solution containing ethanol, isopropyl alcohol or nonoxynol-4.

 6. The composition of claim 5 wherein water constitutes no more than about 20% v/v of the solvent.

30 7. The composition of any of claims 1 to 6 wherein the alkyltrialkoxysilane is present in about 0.5 to 40% v/v based on the total volume of the composition.

1 8. The composition of any of claims 1 to 7 wherein
based on the total volume of the composition
alkyltrialkoxysilane is present in an amount from about 2 to
10% v/v in 98-90% v/v of a solvent.

5 9. The composition of any of claims 1 to 8 wherein
the alkyltrialkoxysilane is octadecyltriethoxysilane,
n-octyltriethoxysilane, 3-aminopropyltriethoxysilane,
vinyltriethoxysilane, n-(triethoxysilylpropyl) urea or
ethyltriethoxysilane.

10 10. A method of strengthening hair comprising the
steps of:

 a., applying to the hair an effective amount of the
composition of any of claims 1 to 9

 b., applying heat to the hair to effect curing.

15 11. The method of claim 10 wherein the hair is an
alkali-weakened hair. .

 12. The method of claim 10 or 11 wherein the hair
is virgin hair.

20 13. The method of any of claims 10 to 12 wherein
prior to step (a) the hair is set to the desired
configuration.

 14. The method of any of claims 10 to 13 wherein
the hair is pre-treated with an alkali or a thioglycolate
prior to applying the composition.

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